



Mineral-char interactions during coal-char combustion investigated

Melissa Lunden, Chris Shaddix, Nancy Yang, and Tom Headley are investigating the nature of mineral/char interactions during pulverized coal combustion, and the effect these interactions can have on char-combustion kinetics. This work is part of Sandia's Coal Combustion Sciences project sponsored by the DOE Office of Fossil Energy, Federal Energy Technology Center's Direct-Utilization Advanced Research and Technology Development Program.


Historically, research on coal-char reactivity has focused on the oxidation kinetics of the carbonaceous organic matrix within the char. However, the distribution of mineral matter within the organic structure can have a strong influence on the global reactivity of the char particle by affecting the density of active carbon sites as well as the pore structure that provides oxygen access to these sites. These effects are of particular importance in late-stage carbon burnout, when the char structure consists of small amounts of carbon in a predominantly ash framework.

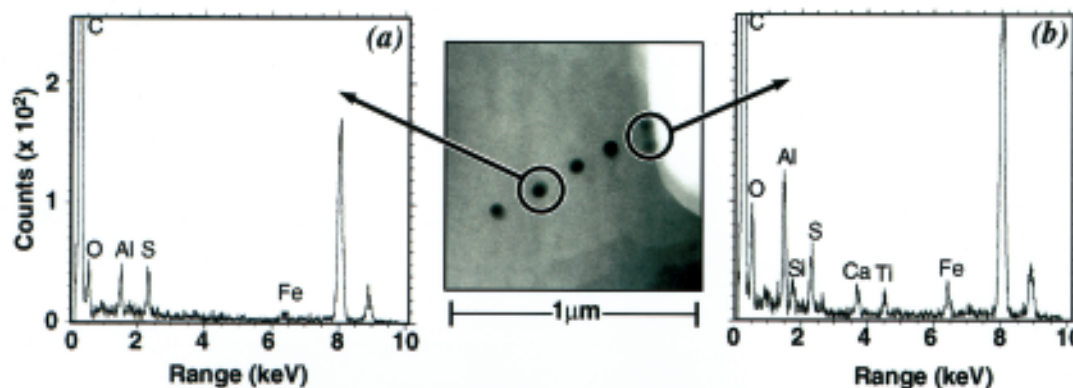
Carbon burnout is an important system-operating parameter in modern pulverized-coal fired boilers, affecting boiler efficiency, electrostatic precipitator operation, and the value of the fly ash as a salable product. The recent incorporation of staged-combustion, low- NO_x coal burners has led to unacceptable amounts of carbon in fly ash in many utility boilers.

Recent modeling of char-carbon burnout kinetics at Brown University and Sandia has shown that an ash inhibition effect on oxidation rates is required to accurately predict experimental measurements of mass loss

during char burnout. To investigate the nature of this inhibition, extensive electron microscopy has been performed on chars of Pittsburgh #8, a high-volatile, bituminous coal, that had been subjected to differing extents of burnout in several high-temperature environments.

High-resolution transmission electron microscopy (HRTEM) of the collected char particles shows a surprising amount of inorganic material in solid solution within the carbonaceous matrix, as detected by energy dispersive X-ray spectroscopy (EDS). Inorganic elements, primarily aluminum, silicon, and iron with some calcium and titanium, are seen at levels of approximately 5 to 10 percent of the total local mass. This atomically dispersed inorganic matter does not appear in the raw coal in significant amounts (< 2 percent).

The figure shows an HRTEM image of the area around an interior pore surface. The EDS spectra show that the amount of inorganic material in solution increases towards the pore wall, at times approaching 20 percent of the total local mass. Not observed previously, this inorganic matter in solution can act as both a microscopic ash film, blocking oxygen access to active carbon sites, as well as a diluent, reducing the total available carbon per surface area in the char. In addition, this inorganic mineral matter may affect the process of carbon turbostratic crystallite growth, and therefore the loss of carbon reactivity by thermal annealing. HRTEM analysis of chars from a coal of similar rank but with poor burnout behavior is currently being performed in order to better elucidate the importance of this phenomena. 



EDS spectra performed in the HRTEM on char samples show an increase in the local concentration of mineral species at the pore surface (b) compared to further inside the char matrix (a). The dark circles on the HRTEM image of the ground char particle show the location of individual EDS measurements. The pore is indicated by the light area in the upper right corner of the image. The char was collected after experiencing 50 percent mass loss (dry-ash free).


Mixtures of explosives separated using microcapillaries

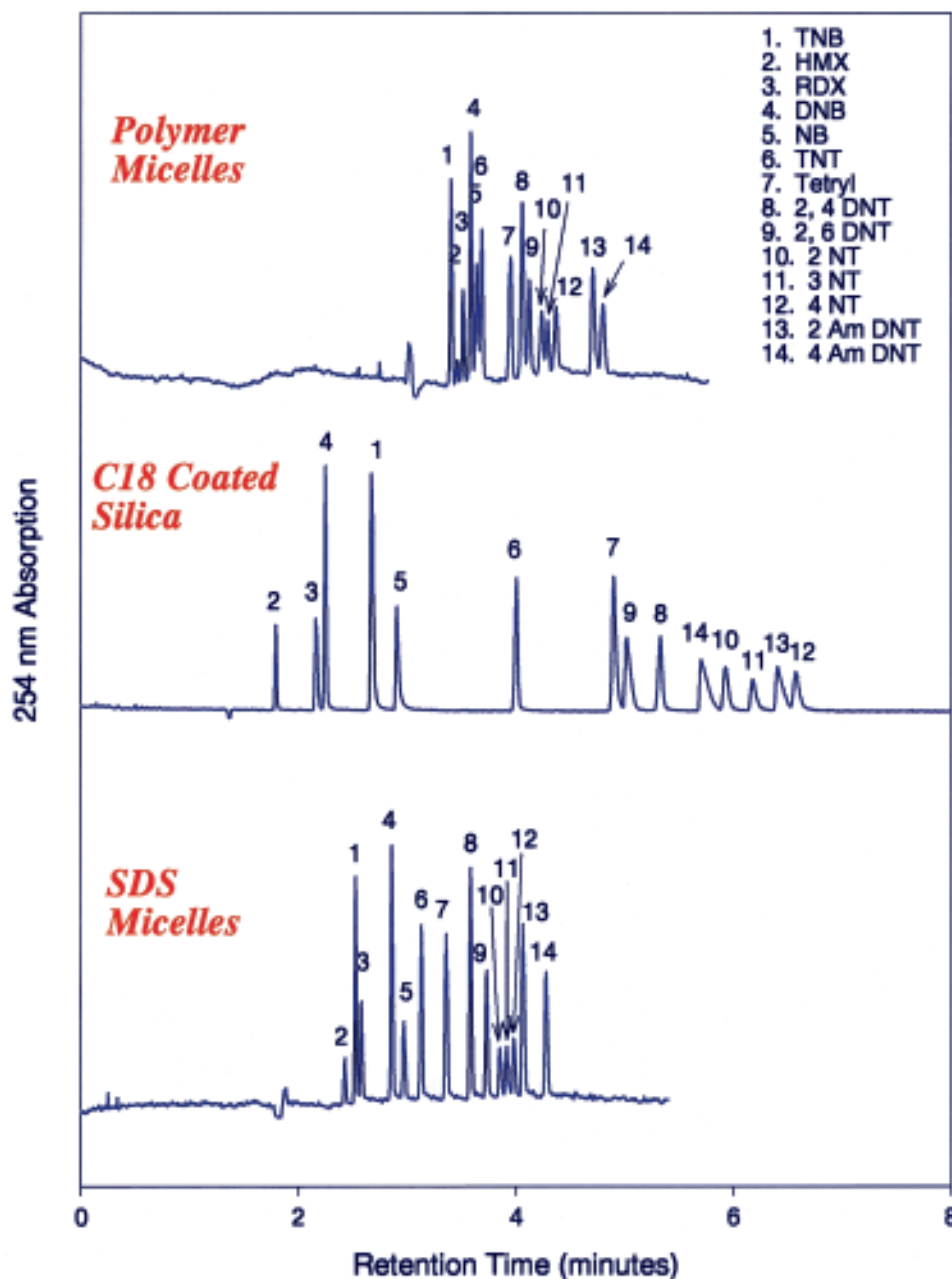
The accurate characterization of complex mixtures of explosives and their degradation products is important in a number of applications such as forensics, health and safety, and environmental remediation. Photolytic and biological degradation of high explosives leads to the formation of a number of closely related compounds that may require positive identification. Traditional characterization techniques based on pressure-driven flow, which may take 30 minutes or more per sample, have proven inadequate to fully resolve these compounds in a single chromatographic run. This necessitates supplemental separation steps, incurring additional time and costs, as well as increasing required sample size, generation of waste, and opportunity for contamination.

Recently, Chris Bailey and Judy Ronglien of Sandia's Chemical and Radiation Detection Laboratory and Chao Yan (Unimicro Technologies, Pleasanton, CA) have addressed the separation of explosives. They have examined the use of microcapillary-based electrokinetically driven separations. In electrokinetically driven separations a small sample of a mixture is introduced into a chromatographic column filled with a separation medium. An electrical potential is applied across the column, inducing the sample to migrate through the separation medium and segregate into individual bands that can be easily detected. This is done without the need for pumps or any moving parts.

The figure shows separations of a mixture of 14 explosives and their degradation products using microcapillary-based electrokinetically driven chromatography.

Each of the three runs is generated independently using a different type of separation medium. The separations fully resolve all of the components of the mixture in a fraction of the time it takes for a partial separation using pressure-driven techniques. The efficiencies – measures of the narrowness of the separated bands – of the electrokinetically driven separations are an order of magnitude or more higher than those typically obtained using traditional chromatography.

The use of microcapillaries with inner diameters of 50 to 100 microns reduces generation of wastes as well as the amount of sample consumed. This can be important in forensic applications where very little sample is available. Each of the separations shown in the figure consumed a few nanoliters of sample that contained a few hundred picograms of each compound. The demonstration of three independent electrokinetic-separation schemes allows for a great deal of flexibility in tailoring to specific applications. For example, running a sample through an array of parallel channels enables highly accurate identification, which would be required for an explosives monitor. 



Microcapillary electrokinetically driven separations of explosives and degradation products. The different chromatograms show results using three different separation media.



Keith Casavant (Cornell U., second from left) recently completed the first portion of a co-op internship working with (left to right) Allen Robinson, Larry Baxter, and Steve Buckley on experiments associated with global climate change, Chernobyl contamination, and energetic materials combustion.



Professor Lorenz Sigurdson (University of Alberta, right) and host Bill Ashurst (left) along with Professor Wolfgang Kollmann (U.C. Davis, not shown) are simulating the vorticity dynamics observed in Professor Sigurdson's experiments of impacting water drops and bursting soap bubbles.

New on the CRF Website: Employment Opportunities, a list of available research positions viewable at www.ca.sandia.gov/crf/crfjobs.html.



Lori Brock (right), a post-doctoral appointee working with Eric Rohlfling (not pictured), has been performing high-resolution spectroscopy on important combustion radicals. She collaborated with Andrew McIlroy (left) and Craig Taatjes (center) to apply her spectroscopic studies to investigations of flame chemistry and chemical kinetics before joining OSRAM SYLVANIA, Inc. in Danvers, MA.

The CRF News is published bimonthly by the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.

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CHEMKIN III available for PCs

San Diego-based Reaction Design has just released versions of The CHEMKIN Collection III for PCs operating Windows 95 or NT, in addition to versions for UNIX systems. Reaction Design plans further enhancements including provision of an up-to-date user interface, an expanded reaction and property database, and a post-processing capability. Collaboration with users in the combustion community will be sought to help guide these improvements.

In February 1997, Sandia granted the right to distribute CHEMKIN to Reaction Design. Since then, 56 licenses have been issued. Reaction Design provides technical support and software updates as a part of its software licensing. Dr. Ellen Meeks, formerly of Sandia and a principal developer of the CHEMKIN III and Surface CHEMKIN III software packages, as well as author of the Aurora stirred-reactor program, recently joined the staff of Reaction Design as Principal Scientist.

For more information about The CHEMKIN Collection III, please visit Reaction Design's web site at www.ReactionDesign.com or send e-mail to CHEMKIN@ReactionDesign.com.

Fuel-air mixing investigated in a gasoline direct-injection engine


Research on gasoline direct-injection (GDI) engines has surged recently due to its potential for increased fuel efficiency coupled with high performance. The current efforts build on previous designs, including Ford and Texaco GDI engines of the 1980s, and take advantage of today's improved fuel injector technology, increased control electronics sophistication, and advanced research techniques including optically accessible engines and laser-based diagnostics. With support from DOE's Office of Advanced Automotive Technologies, Dick Steeper is investigating the important fuel-air mixing process in a GDI engine. The project is part of a Cooperative Research and Development Agreement with Chrysler, Ford, and General Motors (GM).

As the name implies, GDI engines incorporate a fuel injector within each cylinder to gain several advantages. Fuel control is enhanced over conventional, port-injected engines since undesirable fuel accumulations in the intake port are avoided. Evaporative cooling of the air charge is enhanced, leading to improved volumetric efficiency, better knock tolerance, and higher compression ratios. Finally, GDI engines can run ultra-lean by injecting fuel late in the compression stroke; in this strategy, air intake is unthrottled so that air-pumping losses are eliminated. These advantages could lead to fuel efficiency improvements of 20 percent over current spark-ignited engines.

Understanding the fuel-air mixing process is critical to the success of the GDI concept. To investigate this process, Duane Sunnarborg, Jim Boehmke, Lloyd Claytor, and Dick have designed and assembled a research GDI engine. The team started with a GM prototype GDI head and mated it to a transparent, fused silica cylinder with a windowed piston, resulting in a realistic-geometry engine with multi-directional optical access. Using a UV laser sheet to induce fluorescence in liquid- and vapor-phase gasoline, the facility enables imaging of the fuel-air mixing process in cylinder.

A typical laser-induced fluorescence (LIF) image of a fuel-injection event superimposed on a schematic of the GDI engine is shown in Figure 1. Imaging the evolving liquid fuel distribution during and following injection reveals the extent of wall and piston wetting that occurs

under varying operating conditions. This is important information since in-cylinder liquid fuel films can contribute to increased emissions.

Figure 2 is an LIF image of vapor-phase fuel late in the compression stroke. At high-load conditions, a homogeneous fuel-air mixture is required at the time of ignition; the inhomogeneities revealed in this image could lead to misfire. By comparing fuel-air mixture quality derived from LIF data with performance data from a twin (but non-optical) research engine at GM, the project partners will look for insights into GDI engine design and control. 

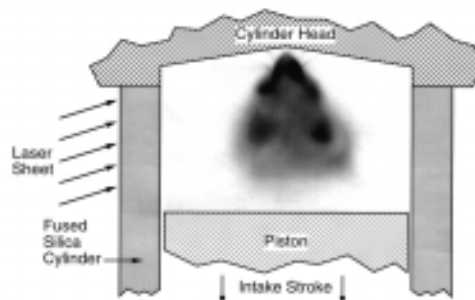


Figure 1. LIF image of liquid fuel during intake-stroke injection. The laser sheet is inclined to illuminate the entire spray. Note that the injection is timed to avoid wetting the receding piston.

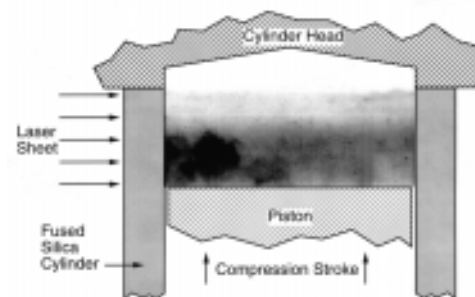


Figure 2. LIF image of vapor-phase fuel during the compression stroke. The dark regions on the left indicate rich fuel pockets being concentrated by the advancing piston.

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